Voltammetric Detection of Drugs Considered as Emerging Pollutant in Water at Carbon Nanofiber Composite Electrode

Magdalena Ardelean[1], Florica Manea[1]*, Anamaria Baciu[1], Aniela Pop[1], Rodica Pode[1].

[1] *"Politehnica" University of Timisoara, Sqr. Victoriei no.2, 300006 Timisoara, Romania, e-mail: florica.manea@.upt.ro*

Abstract

In this study, carbon nanofiber-epoxy (CNF) composite electrode was tested using cyclic voltammetry (CV), differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) techniques for the quantitative determination of naproxen (NPX), which was chosen the model for the anti-inflammatory drugs as emerging pollutants from water. The best performance in relation with the sensitivity and the detection potential value was obtained by employing DPV, and in relation with the lowest limit of detection and quantification was achieved by SWV under operating conditions of modulation amplitude of 0.2V, step potential of 0.05V and a scan rate of 0.025V.

Introduction

Naproxen - *(2S)-2-(6-methilnaphthalen-2-yl) propanoic acid* is a non-steroidal anti-inflammatory drug from the phenylpropanoic acid class, used in the treatment of osteoarthritis, rheumatoid arthritis, degenerative joint disease, ankylosing spondylitis, acute gout and primary dysmenorrhea [1, 2]. This drug belongs to emerging pollutants, which are candidate for the future regulation that requires information about their presence, occurrence, fate and toxicity in the environment.

Various number of studies are directed to drugs, pharmaceuticals and related compounds as emerging pollutants in water, because their presence especial in river water has been reported [3].

One of the most important aspects in order to assess the drugs as emerging pollutants in water is represented by the analytical methods for the quantitative determination of their concentrations. The electrochemical methods should be regarded as feasible alternative due to their simplicity, low-cost, fast and availability for the on-site and in-field detection application. The key for the performance of the electroanalytical method is given by the electrode material and the electrochemical techniques.

Nanostructured carbon based composite electrodes have been reported as very efficient in the electroanalytical detection application [4, 5]. In this study, carbon nanofiber-epoxy composite electrode was tested for the electrochemical detection of naproxen (NPX), which was chosen the model for the drugs as emerging pollutants in water.

Experimental

Naproxen (NPX) was provided by AC Helcor SRL, Romania. A stock solution of 1mM was prepared by using 0.1 M NaOH solution (Merck, Germany).

Electrochemical measurements

The electrochemical performance of this electrode was studied by cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), and square-wave voltammetry (SWV). An electrochemical pre-treatment by three repetitive cyclings from 0 V to +1.25 V vs. SCE in

0.09M Na_2SO_4 and 0.01M H_2SO_4 supporting electrolyte was performed. All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode, and the CNF composite working electrode.

Results and discussion

To develop the voltammetric analytical detection for the quantitative determination of NPX, cyclic voltammograms were recorded on CNF composite electrode in 0.1 M Na_2SO_4 supporting electrolyte in the presence of various NPX concentrations. The results are presented in Figure 1.

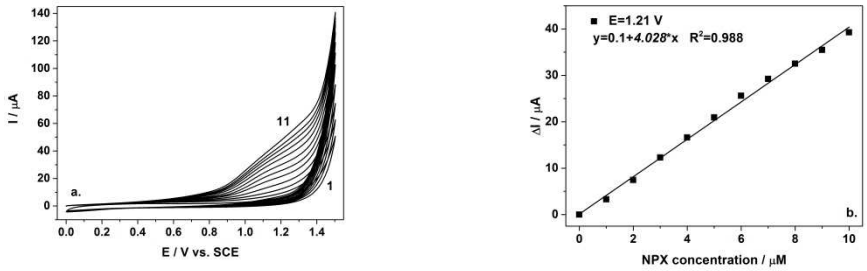

Figure 1. a. Cyclic voltammograms recorded on CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) in the presence of 50 µL 0.1M NaOH (curve 2) and 1-10 µM NPX (curves 3-12), at a potential scan rate: 0.05 Vs^{-1} in a potential range: 0 to +1.5 V/SCE; **b.** Calibration plot of the current vs. NPX concentration of the CVs recorded at E= +1.21V/SCE.

The oxidation process of NPX on CNF electrode started at +0.4V/SCE and the peak current slightly increased until +0.9V/SCE, after which, a more pronounced width peak was noticed. Since the stock solution was prepared by using sodium hydroxide, the influence of the hydroxide was studied and no relevant peaks were noticed. As a precaution, before adding the analyte, a 50µL volume of sodium hydroxide was added into supporting electrolyte. Also, it was noticed the lack of the cathodic peak, suggesting the irreversibility of the oxidation process. A good linearity anodic current vs. naproxen concentration was observed, and for the oxidation potential of +1.21 V/SCE, a sensitivity of 4.028 µA/µM was achieved.

For an improvement in relation with the sensitivity and oxidation potential, differential-pulsed voltammetry was employed. Under the optimized conditions previously determined for other drug determination, *i.e.*, a modulation amplitude of 0.2V, step potential of 0.05V and scan rate of 0.025V/s, a good linearity and a better sensitivity were obtained. In Figure 2 are presented the differential-pulsed voltammograms obtained under these conditions for NPX detection on CNF electrode. In this case, the oxidation process started at about +0.45V/SCE and a well-defined peak was noticed at +0.95V/SCE. In comparison with cyclic voltammetry, the oxidation potential shifted to more negative values for DPV (+0.95V/SCE vs.+1.21V/SCE) and an improved sensitivity was reached (9.959µA/µM vs. 4.028 µA/µM).

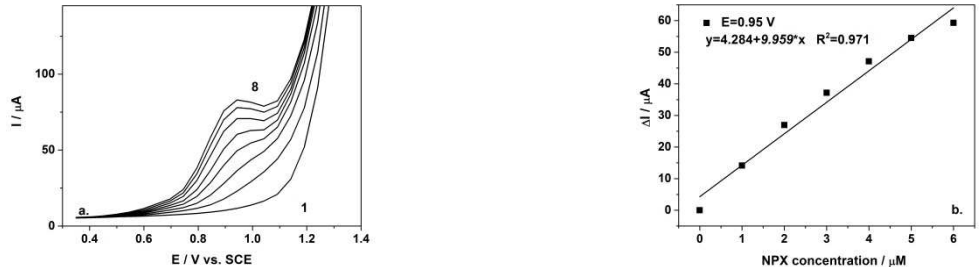

Figure 2. a. Differential-pulsed voltammograms recorded on CNF electrode under operating

conditions: modulation amplitude of 0.2V, step potential of 0.05V and potential scan rate of 0.025 Vs^{-1} between 0.35 and +1.35V/ SCE in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) in the presence of 50 µL 0.1M NaOH (curve 2) and 1-6 µM NPX (curves 3-8); **b.** Calibration plot of the current vs.NPX concentration recorded at E= +0.95V/SCE.

Square-wave voltammetry was employed also, as advanced pulsed technique, in order to compare with DPV results and to find the best voltammetry technique. Also, previous optimization of operating conditions for SWV technique was achieved for other drug detection.

Figure 3. a. Square-wave voltammograms recorded on CNF electrode under operating conditions: modulation amplitude of 0.05V, step potential of 0.005V and a frequency of 10 Hz between 0 and +1.45V/ SCE in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) in the presence of 50 µL 0.1M NaOH (curve 2) and 1-6µM NPX (curves 3-8); **b.** Calibration plot of the current vs. NPX concentration recorded at E= +1.1V/SCE.

By using modulation amplitude of 0.05V, a step potential of 0.005V and a frequency of 10 Hz, sensitivity of 4.366µA/µM was reached (Figure 3b). In comparison with DPV, a slightly shifting to more positive values of oxidation potential was observed (+1.1V/SCE vs. +0.95V/SCE), and also a small decrease of sensitivity (4.366 µA/µM vs. 9.959 µA/µM). This decrease of sensitivity value is explained by the use of small values for operating parameters, *e.g.* modulation amplitude of 0.05V for SWV vs. 0.2V for DPV. The sensitivity obtained for SWV is similar with the one obtained for CV.
In Table 1 are gathered all the electroanalytical parameters obtained for naproxen detection in aqueous media on CNF electrode.

Table 1. Electroanalytical parameters obtained on CNF electrode for NPX detection

Technique	**E_{ox} / V**	**Sensitivity (µA/µM)**	**Correlation coefficient**	**RSD (%)**	**LOD (µM)**	**LOQ (µM)**
CV	1.21	4.028	0.988	5.2	0.133	0.444
DPV	0.95	**9.959**	0.971	4.24	0.146	0.450
SWV	1.1	4.366	0.997	9.01	0.124	0.415

4. Conclusions

Based on the above-presented results, it may be concluded that carbon nanofiber-epoxy composite electrode exhibited the peculiarities for naproxen detection in aqueous media, using voltammetric techniques. The best performance in relation with the sensitivity was obtained by employing DPV under operating conditions of modulation amplitude of 0.2V, step potential of 0.05V and a scan rate of 0.025V. A slight improvement of the lowest limit of detection was achieved using square-wave voltammetry techniques operated at modulation

amplitude of 0.05V, step potential of 0.005V and a frequency of 10 Hz. However, the lowest value of the detection potential and the electroanalytical parameters reclaim the differential-pulsed voltammetry technique the most valuable technique for the detection of naproxen from water on carbon nanofiber composite electrode.

References

[1] P. Norouzi, F. Dousty, M.R. Ganjali, R. Daneshgar, Int. J. Electrochem. Sc. 4 (2009) 1371.
[2] N. Adhoum, L. Monser, M. Toumi, K. Boujlel, Anal. Chim. Acta. 495 (2003) 69.
[3] A. Nikolaou, Pharmaceuticals and related compounds as emerging pollutants in water: analytical aspects, Global NEST J., 15 (2013) 1.
[4] A. Remes, A. Pop, F. Manea, S.J. Picken, J. Schoonman, Sensors. 12 (2012) 7033.
[5] S. Motoc, A. Remes, A. Pop, F. Manea, J. Shoonman, J. Environ. Sci. 25 (2013) 838.
[6] M. Ardelean, F. Manea, R. Pode, Int. J. Pharm. Pharmaceut. Sci., 5 (2013) 318.

Acknowledgements

This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013 and partially by the PNII-165/2011 and PNII-60/2012.